

# PATENT COOPERATION TREATY

14154WO01

P+K  
TAG

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:  
CHRISTOPHER M. SCHARFF  
MCANDREWS, HELD & MALLOY, LTD.  
500 WEST MADISON STREET  
SUITE 3400  
CHICAGO, IL 60661

## PCT

### NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of Mailing  
(day/month/year)

29 MAR 2005

Applicant's or agent's file reference

14154WO01

#### IMPORTANT NOTIFICATION

International application No.

PCT/US03/38735

International filing date (day/month/year)

05 December 2003 (05.12.2003)

Priority date (day/month/year)

20 December 2002 (20.12.2002)

Applicant

STEPHAN COMPANY

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

RECEIVED  
APR 01 2005  
MCANDREWS, HELD & MALLOY

Name and mailing address of the IPEA/US

Mail Stop PCT, Attn: IPEA/US  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

Facsimile No. (703) 305-3230

Authorized officer

Jerry D. Johnson

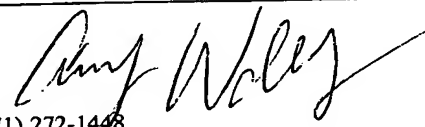
Telephone No. (571) 272-1448

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference  14154WO01	<b>FOR FURTHER ACTION</b>		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No.  PCT/US03/38735	International filing date ( <i>day/month/year</i> )  05 December 2003 (05.12.2003)	Priority date ( <i>day/month/year</i> )  20 December 2002 (20.12.2002)	
International Patent Classification (IPC) or national classification and IPC  IPC(7): C10M 173/02 and US Cl.: 508/480, 482; 72/42			
Applicant  STEPHAN COMPANY			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>3</u> sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of <u>7</u> sheets.</p> <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of report with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input type="checkbox"/> Certain observations on the international application</li> </ul>			
Date of submission of the demand  18 May 2004 (18.05.2004)		Date of completion of this report  07 December 2004 (07.12.2004)	
Name and mailing address of the IPEA/US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230		Authorized officer Jerry D. Johnson  Telephone No. (571) 272-1448	

## I. Basis of the report

## 1. With regard to the elements of the international application:\*

☒ the international application as originally filed.☒ the description:pages NONE as originally filedpages NONE, filed with the demandpages 1-7, filed with the letter of 13 July 2004 (13.07.2004).☒ the claims:pages 9-10, as originally filedpages NONE, as amended (together with any statement) under Article 19pages NONE, filed with the demandpages NONE, filed with the letter of \_\_\_\_\_.☐ the drawings:pages NONE, as originally filedpages NONE, filed with the demandpages NONE, filed with the letter of \_\_\_\_\_.☐ the sequence listing part of the description:pages NONE, as originally filedpages NONE, filed with the demandpages NONE, filed with the letter of \_\_\_\_\_.2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☐ The amendments have resulted in the cancellation of:☐ the description, pages NONE☐ the claims, Nos. NONE☐ the drawings, sheets/fig NONE5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. STATEMENT**

Novelty (N)	Claims <u>NONE</u>	YES
	Claims <u>1-10</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-10</u>	NO
Industrial Applicability (IA)	Claims <u>1-10</u>	YES
	Claims <u>NONE</u>	NO

**2. CITATIONS AND EXPLANATIONS**

Claims 1-10 lack novelty under PCT Article 33(2) as being anticipated by Rieder.

Rieder, U.S. Patent 4,172,802, teaches aqueous metal working fluids exhibiting high lubricity and high stability comprising water and an acid terminated diester of a secondary diol (abstract). There may be added to the metal working composition various additives such as corrosion inhibitors, biocides, fungicides, bacteriocides, surfactants, extreme pressure agents and antioxidants well known in the art in conventional amounts (column 8, lines 9-14). The metal working composition may have therein a concentration of the carboxylic acid terminated diester or the organic salt or alkali salt thereof over a wide range, preferably from 0.10% to 20% more preferably 0.03% to 5% by weight of the weight of water plus the weight of carboxylic acid group terminated diester or organic amine or alkali metal salt thereof (column 8, lines 15-22). In Example 22, column 11 of Rieder, a composition containing 15 gms phthalate ester, 15 gms triethanol amine and 470 gms water is disclosed.

Claims 1-10 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

----- NEW CITATIONS -----

Attorney Docket No. 14154WO01

HYDROLYTICALLY STABLE PHTHALATE ESTER LUBRICANTS AND METHOD  
OF METALWORKING WITH HYDROLYTICALLY STABLE PHTHALATE ESTERS  
LUBRICANTS

RELATED APPLICATIONS

[0001] This Application claims priority to U.S. Provisional Application No. 60/435,071, filed December 20, 2002.

BACKGROUND OF THE INVENTION

[0002] The metalworking industry requires lubricants in many of its operations. Water-based lubricants are particularly desirable because of the ease of using and disposing of the water base. Adipate esters have also been used as successful lubricants in the metalworking industry. Adipate esters, however, are unstable in water solutions and thus less desirable than water-based lubricants. In the past, it has been determined that esters having groups with steric bulk immediately adjacent the ester group may lend some hydrolytic stability to lubricants. The metalworking industry has gone to utilizing isopropyl and 2-ethylhexyl esters as a source of hydrolytic stability due to the steric bulk of the groups adjacent to the ester linkage. However, there continues to be a need for hydrolytically stable lubricants for use in the metalworking industry.

BRIEF SUMMARY OF THE INVENTION

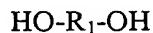
[0003] The present invention provides a hydrolytically stable phthalate ester lubricant and a method of metalworking with a hydrolytically stable phthalate ester lubricant. The phthalate esters used in the present invention have shown superior hydrolytic stability versus other esters and have shown successful lubrication results in ASTM testing for lubricants.

## DETAILED DESCRIPTION OF THE INVENTION

[0004] The phthalate esters that may be used in the lubricant of the present invention include (I) a phthalate polyester-ether polyol, (II) a phthalic anhydride reacted with an equivalent of a fatty alcohol which is then ethoxylated with a variety of moles of ethylene oxide (or propylene oxide), and (III) the amine-neutralized salts of item (II).

[0005] Referring to (I), the phthalate polyester-ether polyol is the reaction product of:

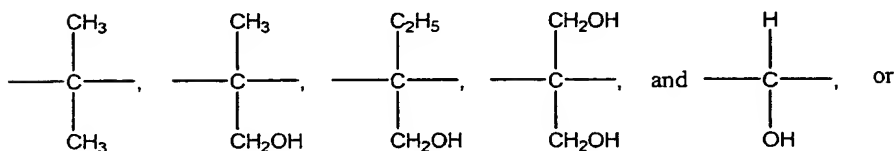
- (1) about 2 – 60 % based on the weight of the polyester-ether polyol of phthalic anhydride or phthalic acid;
- (2) about 40 - 98 % based on the weight of the polyester-ether polyol of at least one polyol of the formula:



wherein  $\text{R}_1$  represents:

- (a) alkylene groups of about 2 to 10 carbon atoms;
- (b)  $-\text{CH}_2\text{-R}_2\text{-CH}_2-$

where  $\text{R}_2$  represents:



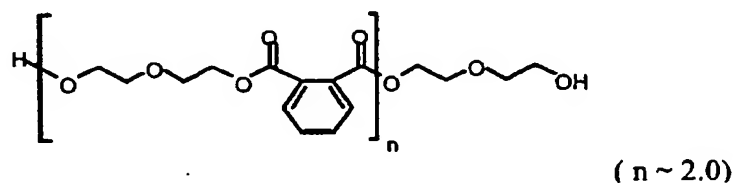
- (c)  $-(\text{R}_3\text{O})_n\text{-R}_3-$

where each  $\text{R}_3$  independently is an alkylene group of about 2 to about 4 carbon atoms, and  $n$  is an integer of from about 1 - 200;  
and

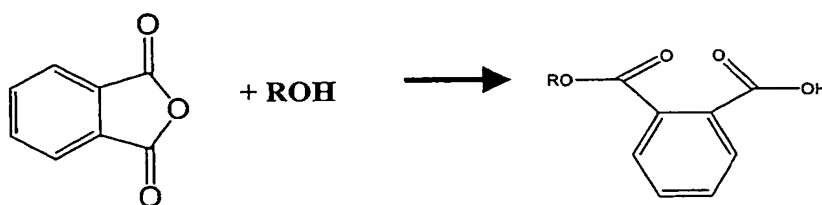
- (3) about 10 – 80 % based on the weight of the polyester-ether polyol of an alkoxyating agent.

1P5A/US

[0006] A preferred phthalate polyester-ether polyol is a propoxylated diethylene glycol-phthalic anhydride-based polyester polyol. The diethylene glycol-phthalic anhydride-based polyester polyol is sold by the Stepan Company under the tradename Stepanol PS-2002. Stepanol PS-2002 has the following structural formula.

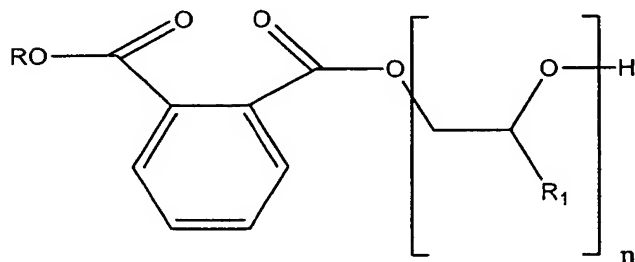


Regarding (II), the phthalic anhydride - fatty alcohol reaction is described as follows.



[0007] where R is C<sub>4</sub> to C<sub>22</sub>, branched or linear.

[0008] The ethoxylation reaction of the product of the phthalic anhydride - fatty acid reaction proceeds by ethoxylating the product with a variety of moles of ethylene oxide (or propylene oxide or butylene oxide) resulting in the following structure.



where R<sub>1</sub> = H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, and n = 1-20, preferably 1-10.

[0009] Regarding (III), the amine-neutralized salts of (II) can also be used as the phthalate ester in the present invention. The amines that may be used to accomplish this

neutralization include triethanolamine, triethylamine, triethanolamine, monoethanolamine, 2-ethylhexylamine, tallow amine ethoxylates or any other amine in general.

[0010] The stability of the phthalate esters of the present invention was investigated in both acidic and basic conditions and compared to adipic ester, a known lubricant often used in the metalworking industry.

[0011] First, testing results of the hydrolytic stability of the propoxylated Stepanpol PS-2002 compared with adipic ester in an acidic system confirmed that the phthalate esters of the present invention provide the hydrolytic stability in acidic conditions desirable for lubricants in the metalworking industry. Specifically, the propoxylated Stepanpol PS-2002 did not exhibit the ester breakdown, and subsequent acid value increase, of the adipic ester.

[0012] Additionally, tests were run which compared the hydrolytic stability of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in a basic system. Base stability can be observed by measuring the breakdown in molecular weight of the ester over time. The breakdown in molecular weight via gel permeation chromatography (GPC) of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in 0.50M KOH and 0.50M TEA (triethyl amine) were calculated by measuring the area percent of the highest molecular weight species in a GPC graph. Testing revealed that the area percent of the adipate polyol decreased drastically over time. In contrast, the area percent of the propoxylated Stepanpol PS-2002 did not decrease over the same time period.

[0013] Third, tests were run to illustrate the hydrolytic stability of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in a KOH system. The average molecular weight of the systems were directly measured to demonstrate the respective stability in a basic system. The average molecular weight of the adipate polyol decreased drastically over time. In contrast, the average molecular weight of the propoxylated Stepanpol PS-2002 did not decrease over the same time period, confirming the hydrolytic stability of the phthalate ester.

[0014] Accordingly, the phthalate esters of the present invention provide the hydrolytic stability in basic conditions desirable for lubricants in the metalworking industry.



IPEA/US

[0015] The lubricant of the present invention was compared to metalworking industry lubricant standards (isopropyl oleate and 2-ethylhexyl oleate). In particular, the tests run were a 4-ball wear, Extreme Pressure Pin and Vee, and a Tapping Torque. All tests were run via an ASTM method.

[0016] Table I sets forth the results for the ASTM D-4172 4-ball wear testing.

TABLE I

Product	Wear Diameter (mm)
Stepan MWA-560 HS	0.598
2-ethylhexyl oleate	0.752
isopropyl oleate	0.628

[0017] Table II sets forth the results for the ASTM D-3233 Extreme Pressure Pin and Vee testing.

TABLE II

Product	Failure Load (lbs)
Stepan MWA-560 HS	1000
2-ethylhexyl oleate	1250
isopropyl oleate	1250

[0018] Table III sets forth the results for the ASTM D-5619 Tapping Torque testing.

TABLE III

Product	Efficiency (%)
Stepan MWA-560 HS	96.20
isopropyl oleate	110.28

[0019] The results as set forth in Tables I, II, and III demonstrate that the lubricants of the present invention provide lubricating properties comparable to those of the metalworking

1PDA/US

industry standards. As such, the lubricants of the present invention may be utilized in any application in the metalworking industry that requires a lubricant such as isopropyl oleate or 2-ethylhexyl oleate.

[0020] A typical lubricant formulation useful in the metalworking industry may consist of up to about 90% water, about 5% phthalate ester, and about 5% triethanolamine. Those skilled in the art recognize that many lubricant formulations are maintained as proprietary trade secret information, and that the phthalate esters disclosed above may be utilized as the main lubricating ingredient in those proprietary lubricant formulations. Thus, the present invention includes such lubricant formulations that utilize the phthalate ester as the main lubricating ingredient. In other words, a person skilled in the art may take his or her proprietary formulation and in the place of the prior main lubricating ingredient utilize the phthalate esters to arrive with a lubricant formulation of the present invention. Such proprietary formulation usually include water, the main lubricating ingredient and at least one other ingredient. The at least one other ingredient may be a single ingredient, as described in the formulation above where the at least one other ingredient is triethanolamine, or may include any number of components.

[0021] Typical water-based lubricants presently include water in an amount between about 60% and about 93% by weight of the total composition, preferably about 75 to about 87%, and a main lubricating ingredient in an amount between about 2% and about 20% by weight of the total composition, preferably about 5 to about 10%. The phthalate esters disclosed above may be used as the main lubricating ingredient in such water-based lubricants and in such amounts. Typical water-based lubricants presently further include at least one other ingredient in a total weight of about 2% and about 20% based on the final composition. One typical component of the at least one other ingredients is an amine in an amount of between about 2% and about 10% by weight of the total composition. The amine is typically used to regulate the pH of the lubricant. Thus, the phthalate esters disclosed above can be used in presently used lubricants by replacing the main lubricating ingredient in those present day lubricants with the disclosed phthalate esters to provide the lubricant of the present invention.

[0022] The phthalate esters disclosed above may also be used as the main lubricating ingredient in such water-based lubricants including this at least one other ingredient.

[0023] The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will occur to others upon the reading and understanding of the specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or equivalents thereof.